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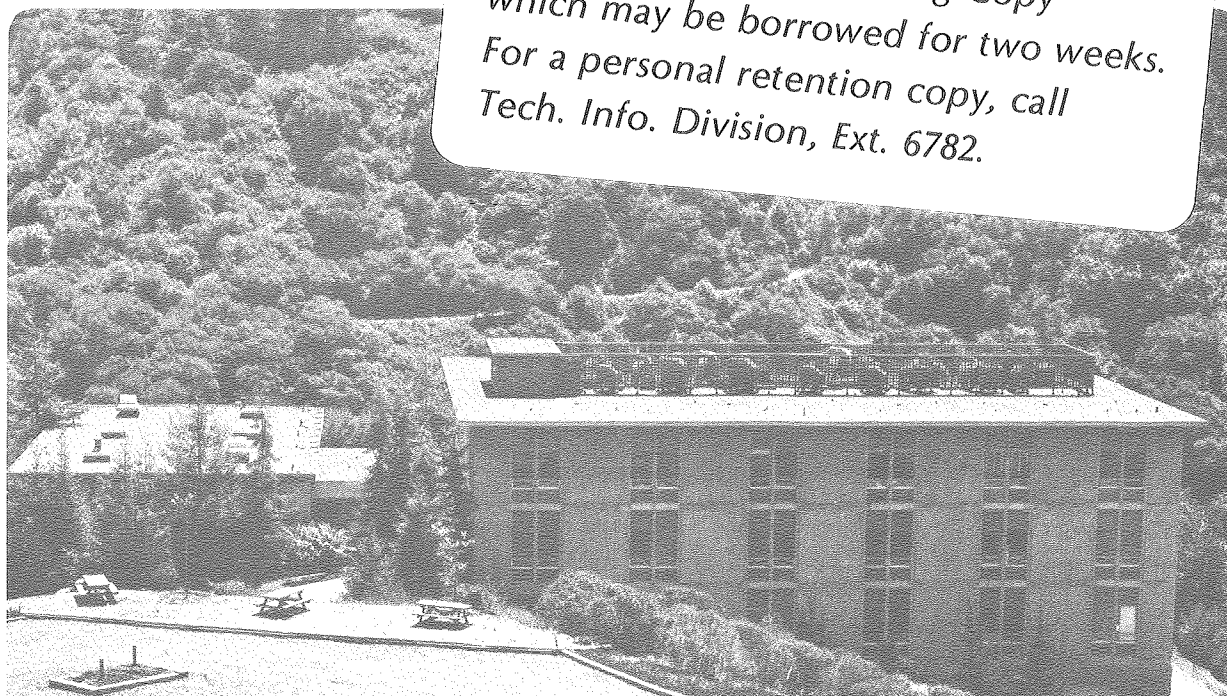## Materials & Molecular Research Division

ANALYTIC POTENTIAL FUNCTIONS FOR WEAKLY BOUND
MOLECULES.   IV. Ar_2 FROM SCATTERING AND SPECTROSCOPIC
DATA

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Analytic Potential Functions for Weakly Bound

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and Spectroscopic Data

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ABSTRACT

The interatomic potential energy function for Ar_2 $X^1\Sigma^+$ has been obtained by inverting the spectroscopic constants of Colbourn and Douglas to the parameters of the Thakkar potential function. This nominal inversion was found to give a potential which did not reproduce the elastic differential cross-section of Lee, et al., with high accuracy. By adjusting the Thakkar potential constants within their calculated spectroscopic uncertainties, good agreement with the differential cross-section was obtained. Both Thakkar functions were used to compute the second virial coefficient for Ar, and the adjusted function was found to give the second virial coefficient to greater accuracy than other Ar_2 potentials over the range 80-1000K. The major fault with the derived potential is in the repulsive wall, but only at energies above twice the well depth. The conclusion is that the Thakkar function can be used to represent not only bound states of weakly bound molecules, but also scattering and bulk phenomena.

INTRODUCTION

The Ar_2 molecule has been the subject of intense study as a prototypical van der Waals or weakly bound molecule. Numerous analytic potentials have been suggested[1] for the interatomic potential function of Ar_2, ranging from simple Lennard-Jones (12,6) functions to quite complex multiparameter functions. Of course, as the number of parameters is increased in any flexible potential function, one should expect increasingly better agreement between observations and theory. Such is the case for Ar_2; potential functions now exist which simultaneously give good agreement with the observed bound levels of Ar_2, the Ar-Ar differential elastic cross-section, and many bulk properties such as the viscosity coefficient and the second virial coefficient.

The primary drawback of such complex potential functions is the difficulty one has in interpreting their parameters in a physically meaningful way. If the function is constructed to give a physical representation of some effect over certain distances, such as the (known) long-range dispersion potential, then one is faced with the arbitrary decision of where and how to terminate this behavior. If the function is merely a multiparameter one with sufficient flexibility to allow the shape of the potential to vary in arbitrary ways, then a physical interpretation of the parameters becomes difficult. Without this interpretation, one loses the opportunity to

compare bonding trends among molecules in any systematic and detailed way.

We have recently shown, for a variety of molecules, that the intermolecular potential for weakly bound molecules can be given with fair[4] to exceptional[2,3] accuracy by the Thakkar function[5]

$$V(R) = e_o \lambda^2 [1 + \sum_n e_n \lambda^n] \qquad (1)$$

where

$$\lambda = 1 - (R_e/R)^p,$$

the parameters e_n are truncated at some maximum n according to the amount of data available, and the parameter p is a positive number, but not necessarily an integer. As we have done before, we chose p by the criterion[5]

$$p = -\frac{R_e \ell_e}{3k_e} - 1 = -a_1 - 1$$

where k_e and ℓ_e are the second and third derivatives of the potential evaluated at the equilibrium separation R_e, and a_1 is the first potential correction constant of the Dunham potential.[6] This choice forces $e_1 = 0$.

Not only is the Thakkar function frequently quite accurate, it has parameters which can be directly related to the equili-

brium mechanical constants of the molecule and to the long range attractive tail of the interatomic potential. These features allow weakly bound molecules to be compared to chemically bound molecules in new ways[7] and lead to new ways of characterizing the bonding among the family of weakly bound molecules.[8]

Our previous applications of the Thakkar function have been limited to bound state spectroscopic inversions. This analysis of Ar_2 allows us to ascertain the suitability of Eq. (1) for calculations of scattering data and bulk properties as well. Bickes and Bernstein[9] have used the Simon-Parr-Finlan (SPF) potential (which is simply a Thakkar potential with $p \equiv 1$ and $e_1 \neq 0$) in a regression scheme for analyzing the differential elastic cross section. Due to the implied (forced) choice of p, the SPF potential can not reproduce the long range part of the potential function. In general, one must "attach" a long range analytic function to functions such as the SPF potential to obtain a well-behaved representation of the true potential. How and where one does this are not uniquely answerable questions. For the Thakkar function, these questions need not arise.

Our goal in this paper is not so much to improve existing potentials for Ar_2 (although in some ways we have) as it is to ascertain the suitability of the Thakkar function for purposes of scattering inversions and bulk property calculations and to include Ar_2 among those molecules which have been analyzed by this method.

METHOD

Briefly, we have inverted spectroscopic data for Ar_2 $X^1\Sigma_g^+$ to a nominal set of Thakkar potential constants. These constants were used to generate the elastic differential cross-section for Ar, and a refinement was indicated. Slight adjustment of these constants gave a refined set of constants in accord with both spectroscopy and scattering. Finally, the second virial coefficient was calculated and found to be in excellent agreement with experiment.

We begin with the spectroscopic constants for Ar_2 reported by Colbourn and Douglas.[10] These constants were obtained from their numerical potential which was derived from a modified RKR procedure. We consider their potential to be the best description of the bound portion of the Ar-Ar interaction. Although we could have fit our initial Thakkar function to their tabulated values, we have chosen instead to use methods consistent with our previous work. The ground state constants, G_v and B_v, were used in a least squares fit to the Dunham energy expression

$$E(v,J) = \sum_{i,j} Y_{ij} (v + 1/2)^i [J(J + 1)]^j$$

and the Y_{ij}'s were used to generate the nominal Thakkar potential constants. These constants are given in Table I along with the statistical uncertainties of each. Due to the complexity of

the spectrum and the small rotational constant of Ar_2, there
are data on only $v''=0-5$ and these are somewhat uncertain, as
described in Ref. 10.

Because of the relative uncertainties in the data and
the low number of degrees of freedom (i.e. the difference be-
tween number of data and number of fitted parameters) in the
least-squares fit, even a minimal set of Y_{ij}'s had fairly high
standard deviations.[11] This in turn caused large statistical
uncertainties in the nominal Thakkar constants. In particular,
the well depth, D_e, is uncertain by 18% (actual error < 10%).
Moreover, not all the available spectroscopic data could be
used since our algorithm used to determine the Thakkar constants
does not employ D_v's, i.e. Y_{2j}'s. It was therefore predictable
that the nominal Thakkar potential could not reproduce the spec-
troscopic data to the accuracy known, even though the primary
descriptors of the potential such as R_e and D_e were in reason-
able agreement with many other measurements.[1] This suggested
that we should go beyond our usual methods of generating this
function and employ other sources of data.

Thus we have used this nominal potential to generate a
differential elastic scattering cross-section for Ar for com-
parison with the high resolution data of Parson, Siska, and
Lee.[12] The comparison is given in Fig. 1b. A qualitative
glance at this figure shows that the agreement is not satis-
factory. The calculated rainbow scattering appears at too
large an angle, indicative of too deep a potential well.

The nominal constants were then systematically varied

throughout their calculated uncertainties in an attempt to improve the differential cross-section. This adjustment was not done in a least-squares fitting sense; rather a set of calculations was made for various parameter values and the RMS deviation of the calculation from the experimental data was iteratively lowered until the agreement was significantly improved. Thus, it is possible that these refined constants could be more highly refined by methods such as suggested by Bickes and Bernstein,[9] but the rapid convergence of our iterative method made further refinement unwarranted.

We give the refined potential constants in Table II, and plot the differential cross section computed from these constants in Fig. 1c. We also show the differential cross-section computed using the Morse-Spline-van der Waals (MSV III) potential of Parson, Siska, and Lee[12] in Fig. 1a. All calculations shown in Fig. 1 were done with the same degree of angular and velocity averaging to allow easy visual comparison among the fits. As a result, the symmetry oscillations at large angles are somewhat artificially enhanced by incomplete averaging.

The refined constants of Table II are remarkably similar to the nominal constants of Table I, but the improvement evident between Fig. 1b and Fig. 1c is rather dramatic. While the MSV III potential gives better agreement at scattering angles slightly less than the primary rainbow, the overall fits of the refined Thakkar potential and the MSV III potential are comparable.

As a final check of the validity of the refined Thakkar

potential, we have calculated the second virial coefficient using the standard expression including the first quantum correction.[13] The results of these calculations for the nominal Thakkar, the refined Thakkar, the MSV III and the Colbourn and Douglas potentials are shown in Fig. 2, as a plot of differences from the experimental data of Levalt Sengers, et al.[14] For this calculation we have connected the table of points given by Colbourn and Douglas with spline functions and extended the potential in regions outside of their table with a Morse function and with the expression

$$V(R) = -\frac{C_6}{R^6} - \frac{C_8}{R^8}$$

at short and long ranges, respectively. The average RMS deviations, evaluated every 100K, of the refined Thakkar, MSV III, and Colbourn and Douglas potentials are 2.06, 2.34, and 1.17 respectively. When calculated every 2K from 80K to 120K the average RMS deviations are 3.84, 8.41, and 4.46. The low deviations for the potential of Colbourn and Doublas are of no surprise since they had adjusted their values of D_e and C_8 to improve agreement between experimental and calculated second virial coefficients.

DISCUSSION

In Fig. 3, we plot the four potentials for Ar_2 of most immediate concern. These are the nominal and refined Thakkar

potentials, the MSV III potential,[12] and the Colbourn and Douglas potential.[10] The refined Thakkar potential has a well depth, D_e, of 100.37 cm^{-1}. Other Ar$_2$ potentials have well depths only slightly less than this. Colbourn and Douglas arrive at 99.55 cm^{-1}. Parson, Siska, and Lee report 100.3 cm^{-1} (MSV II) and 97.83 cm^{-1} (MSV III). The potential of Barker, Fisher, and Watts[1] (not shown in Fig. 1) has D_e = 98.76 cm^{-1}.

The equilibrium separation of Ar$_2$ is quite accurately fixed by Colbourn and Douglas's data at 3.759 ± 0.005 Å. The MSV III potential R_e is 3.760 Å; the Barker, Fisher, and Watts R_e is 3.7612 Å.

Therefore, these most recent and elaborate functions, including the refined Thakkar potential, are in excellent agreement regarding these two main parameters of the inter-atomic potential. They disagree mainly in the shape of the repulsive wall at energies several times the well depth. The Thakkar potential rises much more steeply than a Morse function, while both the MSV and the Colbourn and Douglas potentials have single Morse function repulsive walls.

It is, however, noteworthy that the MSV and Thakkar functions begin to deviate only at energies of ~300 cm^{-1}. The collision energy used in the scattering measurements of Ref. 12 was only 500 cm^{-1}. Colgate, et al.,[15] reported high energy Ar-Ar scattering results which are in much better agreement with the exponential (Morse-like) repulsion of the MSV potential than with the Thakkar potential. We conclude that the repulsive wall of the Thakkar function is in serious error, but only at

energies of several times the well depth.

While the repulsive wall is not well determined above some energy (and probably so for all the potentials discussed here), it is interesting that the refined Thakkar function gives the best calculated second virial coefficient at high temperatures (Fig. 2). The repulsive wall tends to dominate B(T) more at these temperatures, which are well above the Boyle temperature of ca. 400K.

Finally, we list in Table III the energies of the bound vibrational levels, G_v, and the corresponding rotational constants, B_v, for the potentials. The G_v's were computed by numerical solution of the radial Schroedinger equation. Using the resulting wavefunctions for each vibrational level, the B_v's were calculated by the expression

$$B_v = B_e R_e^2 \langle v/R^{-2}/v \rangle .$$

The MSV III potential has been similarly analyzed by Docken and Schafer.[16] We have repeated their calculation in order to have a consistent evaluation of the B_v's and to extend their precision.

The experimental quantities are for the Colbourn and Douglas (CD) potential for $v = 0-5$. The refined Thakkar and the MSV III B_v values agree with the CD values to better than 0.001 cm^{-1}, well within the spectroscopic uncertainty. The G_v values, or more correctly, the level spacings ($\Delta G_{v+1/2}$) are

in similarly good agreement. The MSV III $\Delta G_{v+1/2}$'s are uniformly smaller than the CD values by, on average, -0.29 cm^{-1}. The refined Thakkar $\Delta G_{v+1/2}$'s are both greater and smaller than the CD values. The average error is only -0.01 cm^{-1}. (These quantities for the Barker, Fisher, and Watts potential are given in Table IV of Ref. 9. They are in slightly worse agreement than the MSV III quantities. These quantities for the Bickes and Bernstein SPF potential are: average error = -0.28 cm^{-1}, RMS error = 0.75 cm^{-1}.)

We note that, in Table III, B_5 for the potential of Colbourn and Douglas (0.0289 cm^{-1}) differs from the one listed in Table I of their paper (0.0298 cm^{-1}). Since there were only eight rotational levels determined for v=5, we feel that, although Colbourn and Douglas' B_5 and D_5 fit their data in the least squares sense, their B_5 is a fitting constant and not the true mechanical constant. This problem is similar to the one we cited in determining the Y_{ij}'s for our nominal Thakkar function.

We feel it is important to note also that the Ar$_2$ potential does not behave solely as R^{-6} in the region where the spectroscopic data are pertinent. The objective of any potential function should be to behave correctly in the region of interest. So, although it is true that the refined Thakkar function approaches $R^{-5.6}$ at large separations, the higher order terms correct for the misbehavior of the leading term at the intermediate distances where data are available. The Thakkar potential probably overestimates the degree of binding of v=8, but

this appears academic.

It is apparent from Table III that v=8 is the highest
level of the CD and MSV III potentials, bound by 0.00037 cm^{-1}
and 0.00025 cm^{-1} respectively. This agrees well with v_D=8.27
of Le Roy[17], who used his long-range analysis[18] of Tanaka's
earlier Ar$_2$ absorption data.[19] We repeated this analysis using
Colbourn and Douglas' data, finding v_D=8.32±0.6 and D_e=99.55±
.40 cm^{-1}. It is somewhat surprising that D_e agrees so well
with CD's value since the analysis requires that the potential
be predominately R^{-6}. Indeed the R^{-8} contributions to the bind-
ing at the outer turning points of v=4 and 5 are still 18% and
15%, respectively.[20]

The conclusions to be drawn from these comparisons of the
well and long range tail regions of this potential should
apply in general to the potential functions of other weakly
bound molecules. It is an error to assume p≡6 in the Thakkar
inversion since, on the one hand, the potential never behaves
as a purely R^{-6} function in regions for which one will have
data and, on the other hand, p is directly related, in a clear way,
to properties of the equilibrium region of the potential. One
thereby gains new data on the detailed shape of the potential
function at R$_e$ by making p a free parameter, unconstrained by
any long-range expectations. Thus the value of the Thakkar
inversion is two-fold. First, it provides an accurate analytic
form for the potential well region and the long range tail,
a form which is suitable for both bound state and continuum
properties. And second, it provides new and readily interpret-

able parameters of the weak bond beyond the simple bond length-bond strength parameters. It provides the best comparison from molecule to molecule of the differences in the shape of the potential function in the well region, and it does so without any assumptions as to the extent of validity of piecewise analytic forms, such as the inverse R long range expansion.

CONCLUSIONS

We have shown that the Thakkar potential function for Ar_2 is capable of accurately reproducing the observed spectroscopic levels, differential elastic scattering cross section, and bulk second virial coefficient. Our method relied on the use of spectral data to provide the initial values for the six parameters (R_e, p, e_o, and e_2-e_4) of the analytic function. The scattering data were used to refine these initial values, resulting in a highly accurate function which is free of any splined regions or joined functions.

The repulsive wall at energies several times the well depth is not in accord with high energy Ar-Ar scattering measurements, but the disaccord does not seem to inhibit the ability of the function to predict high temperature bulk properties. The true nature of the repulsive wall should therefore be considered still poorly known. Aside from the fact that both an exponential repulsion and an inverse power law repulsion fail at very high energies (since neither satisfies the R=0 constraints imposed by the virial theorem[7]), there is greater

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reason to assume an exponential shape at these high energies.

The refined Thakkar potential gives $D_e = 100.37$ cm^{-1} with an estimated error of ± 0.3 cm^{-1}, or a D_0 of 84.96 cm^{-1}. The long range tail is, at most, 0.4 cm^{-1} different from the van der Waals tail of the MSV III (or MSV II) potential[11] which is based on theoretical estimates of the C_6 and C_8 coefficients. This difference occurs in the vicinity of $R/R_e = 1.8$. The steeply rising repulsive wall does not deviate significantly from a Morse repulsion until the repulsive potential has risen to ca. 200 cm^{-1}.

ACKNOWLEDGEMENTS

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Table I. Nominal Thakkar potential constants for Ar_2.
The uncertainties relate to the final digits
of the respective constants.

$$R_e = 3.7576(50) \text{ Å}$$

$$B_e = 0.0597676 \text{ cm}^{-1}$$

$$\omega_e = 31.22802 \text{ cm}^{-1}$$

$$e_o = 134.12(10.90) \text{ cm}^{-1}$$

$$p = 5.515 \ (152)$$

$$e_2 = -0.2045 \ (555)$$

$$e_3 = -0.0888 \ (156)$$

$$e_4 = 0.1059 \ (303)$$

$$D_e = 108.99(19.72) \text{ cm}^{-1}$$

Table II. Refined Thakkar potential constants for Ar_2.

$$R_e = 3.758 \text{ Å}$$

$$e_o = 140.38 \text{ cm}^{-1}$$
$$p = 5.62$$
$$e_2 = -0.235$$
$$e_3 = -0.07$$
$$e_4 = 0.02$$

$$D_e = 100.37 \text{ cm}^{-1}$$

Table III. Vibrational energy levels, G_v, and rotational

constants, B_v, for various Ar_2 potentials.

All values are in cm^{-1}.

	G_v			
v	Nominal Thakkar	Refined Thakkar	$CD^{[a]}$	$MSVIII^{[b]}$
0	14.87	15.41	14.80	14.58
1	40.58	41.92	40.53	40.07
2	61.09	62.58	60.94	60.21
3	76.93	77.82	76.55	75.28
4	88.74	88.27	87.46	85.91
5	97.16	94.79	94.24	92.59
6	102.81	98.35	97.85	96.14
7	106.26	99.91	99.28	97.55
8	108.09	100.35	c	c

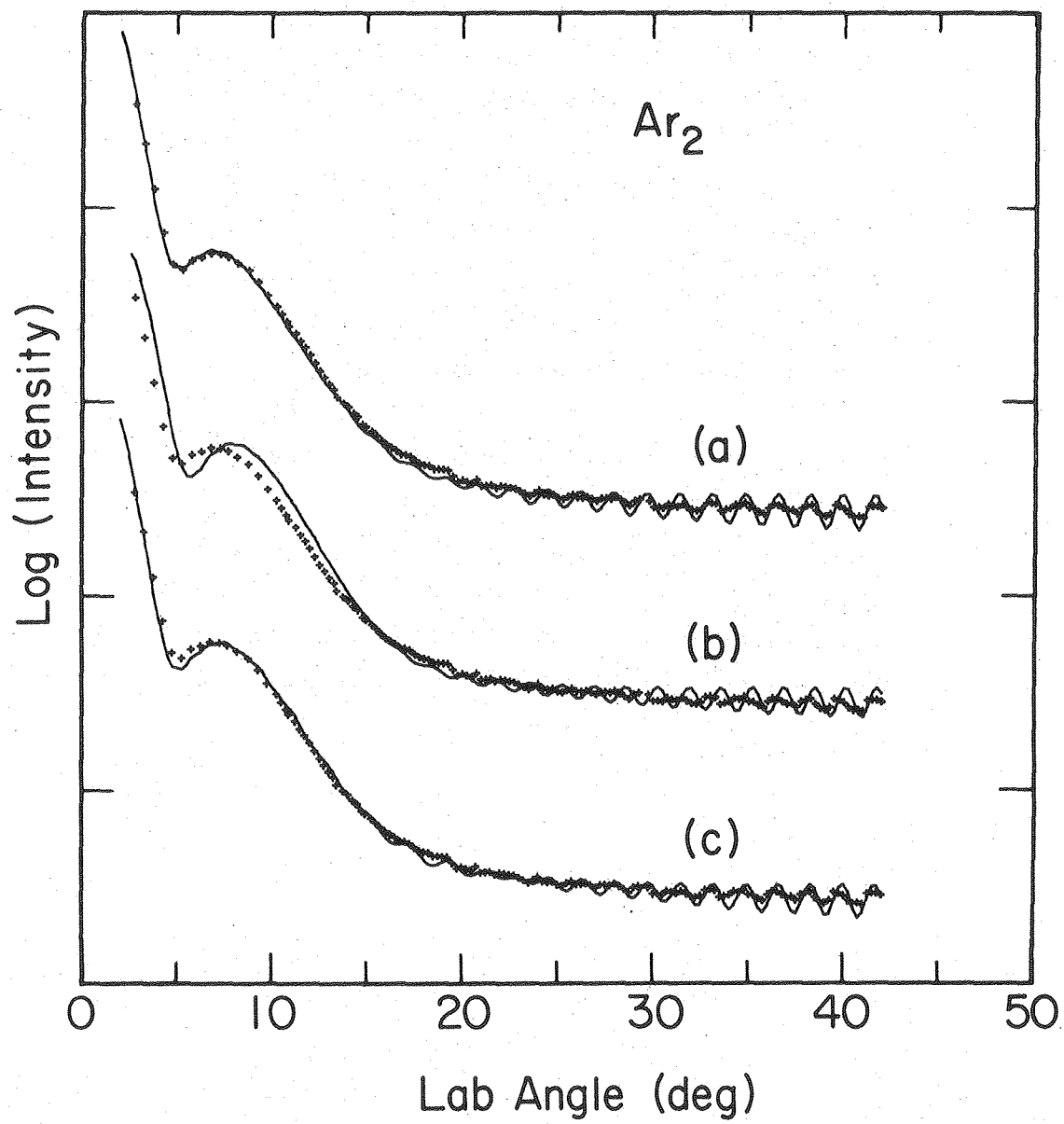|	B_v			
0	0.057778	0.057795	0.057777	0.057758
1	0.053379	0.053439	0.053359	0.053491
2	0.048507	0.048351	0.048467	0.048329
3	0.043279	0.042486	0.042841	0.042718
4	0.037779	0.035872	0.036400	0.036267
5	0.032053	0.028623	0.028904	0.028870
6	0.026127	0.020919	0.020740	0.020706
7	0.020025	0.012935	0.011789	0.011709
8	0.013795	0.004812	0.001370	0.001225

a) Colbourn and Douglas potential of Ref. 10.

b) Scattering potential of Ref. 11. See also Docken and Schafer, Ref. 15.

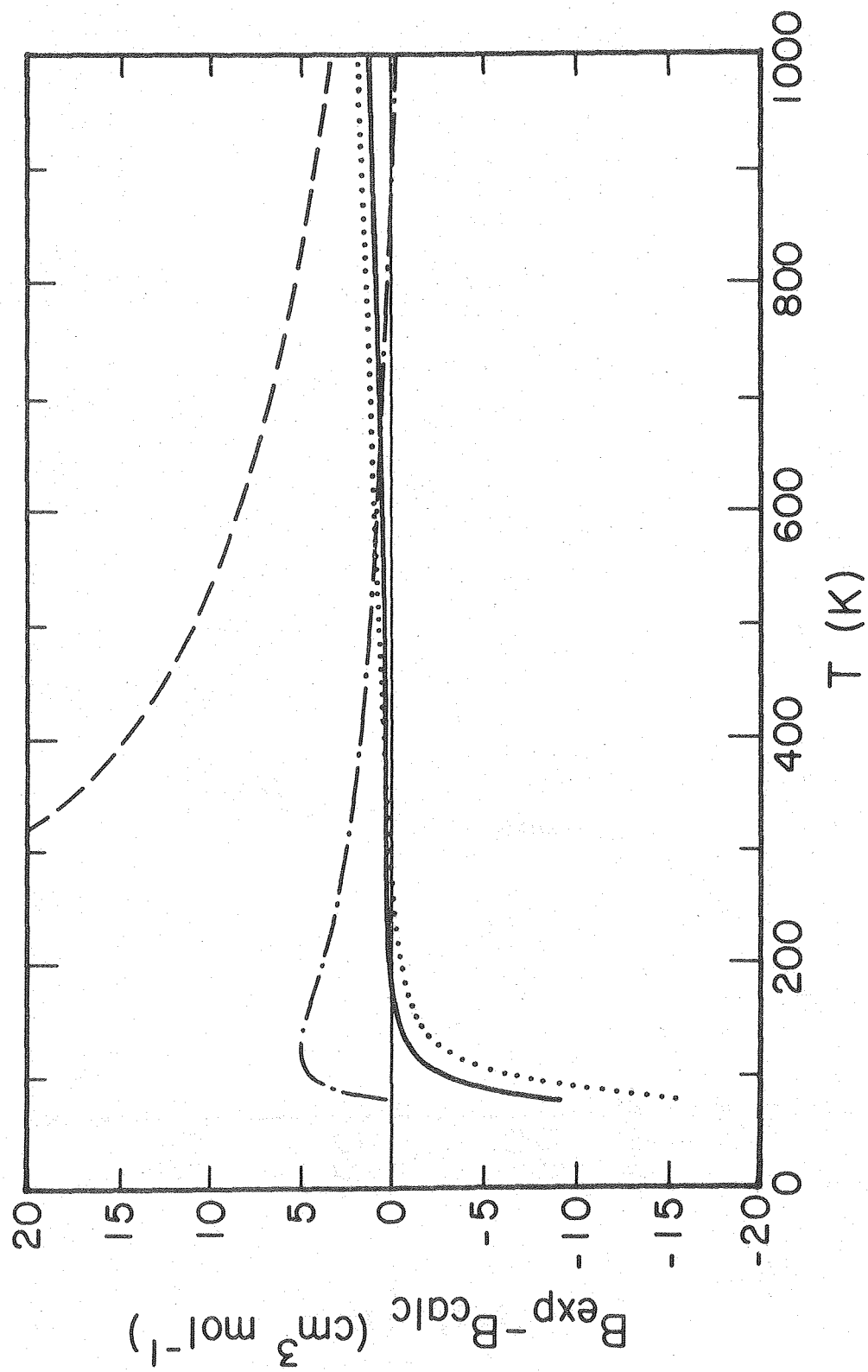c) v=8 is bound by less than 0.001 cm^{-1}.

FIGURE CAPTIONS

Figure 1.   Calculated elastic differential cross sections for
            Ar compared to the measurement of Ref. 11. Curve
            (a) is calculated using the MSV III potential; curve
            (b), the nominal Thakkar potential; curve (c), the
            refined Thakkar potential.

Figure 2.   Deviations of calculated second virial coefficients
            for Ar from the measurements of Ref. 13. Curves are
            for the CD potential (——), the MSV III ($\cdots$), the
            nominal (---) and refined (-·-) Thakkar potentials.

Figure 3.   Comparison of the CD potential (——), the MSV III
            potential ($\cdots$), the nominal Thakkar potential (---),
            and the refined Thakkar potential (-·-) for Ar_2.
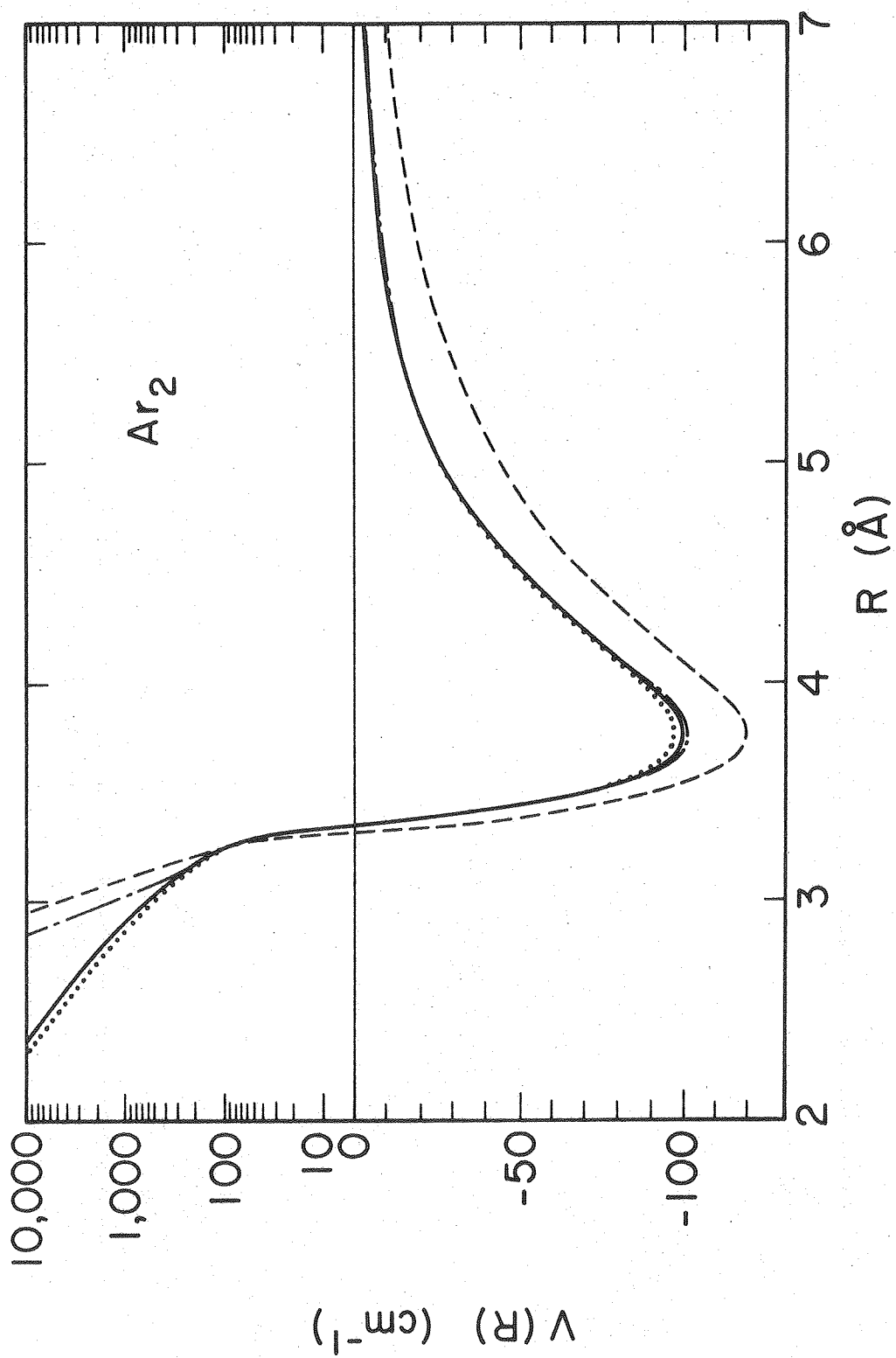   Note the change in the ordinate scale at 10 cm^{-1}.

Figure 1

XBL 811-7708

Axis label (y-axis): $B_{exp} - B_{calc}$ (cm^3 mol^{-1})

Axis label (x-axis): T (K)

XBL 811-7706

Figure 2

Ar$_2$

R (Å)

V(R) (cm^{-1})

XBL 811-7707

Figure 3